A novel electro-catalytic membrane contactor for improving the efficiency of ozone on wastewater treatment

Kuiling Li[a,b], Lili Xu[a,b], Yong Zhang[a,b], Aixin Cao[a], Yujue Wang[c], Haiou Huang[d], Jun Wang[a,b,*]

[a] State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, 18 Shuangqing Road, Beijing, 100085, China
[b] University of Chinese Academy of Sciences, 19 Yuquan Road, Beijing, 100049, China
[c] School of Environment, State Key Joint Laboratory of Environmental Simulation and Pollution Control, Tsinghua University, Beijing, 100084, China
[d] School of Environment, State Key Joint Laboratory of Environmental Simulation and Pollution Control, Beijing Normal University, No. 19, Xinjiekouwai Street, Beijing, 100875, China

A B S T R A C T

A novel electro-catalytic membrane contactor was designed to break the two constrains in O_3 wastewater treatment technology simultaneously: the mass transfer of O_3-water and the decomposition rate of O_3 into ·OH. In the electro-catalytic membrane contact ozonation (ECMCO) process, O_2 and O_3, in the gas chamber, diffuse through the hydrophobic membrane into the water phase; O_2 is electro-reduced to H_2O_2 that catalyzes O_3 producing ·OH to degrade organic compounds rapidly. The removal rate of nitrobenzene (NB) was significantly improved by the combination of membrane contactor and electro-catalytic process. The removal rates of NB in 120 min were 85%, 55% and 23% for ECMCO, membrane contact ozonation and electrolysis, respectively. O_3 concentration and current density had positive effects on the removal of NB, which was related to the accumulated H_2O_2 concentration in aqueous phase. Gas flow had slight positive effects on NB removal when it was lower than 50 mL/min. The pH of the feed may affect the production and the form of H_2O_2 and hence the removal of NB. The highest removal rate in 120 min was up to 95.7% at the initial pH of 4.5. Mass transfer and electrolysis are synthetic in ECMCO process. On one hand, the mass transfer of O_3 increased by 2 times due to the electro-catalytic production of H_2O_2. On the other hand, the existence of O_3 promoted the production of H_2O_2. ECMCO has great potential on promoting mass transfer and decomposition of O_3 into ·OH for the industrial application of O_3.

1. Introduction

Ozone (O_3) can react with many organic compounds due to its high oxidation potential. It has been applied to disinfection and oxidation of drinking water and wastewater for decades [1–3].Although O_3 has been used on water treatment for a long time, the cost of industrial application of O_3 is still high [4]. Two main reasons are that the mass transfer efficiency between O_3 and water is not high enough and the reaction rate between O_3 and ozone-resistant compounds is poor [5,6].

O_3 can't be stored and has to be generated on site when it is needed, because it is easy to decompose to oxygen (O_2). O_3 is generally produced under high voltage discharge using air or O_2 as resources. Normally O_3 is no more than 10% in the effluent of an ozonator and the O_2 in the effluent (~90%) is scarcely used [7]. The low proportion of O_3 in the gas phase determines a weak driving force for O_3 diffusing into liquid phase. The dissolved O_3 also easily escapes from the liquid into ambient environment due to its very low partial pressure in the air (Henry's low) [8]. Besides, the limited bubble surface provides insufficient contact interface area for mass transfer in the conventional contactors [9,10]. These factors determine the poor utilization of O_3. In order to achieve the requirement of oxidation, an excess amount of O_3 has to be provided and the operation cost is usually high. The low production rate and the low partial pressure of O_3 can hardly be changed, while to enlarge the contact interface in unit volume to promote mass transfer of O_3 is a feasible method [11].

Membrane contactor is considered to be able to provide enormous interfacial area in unit volume for O_3 transfer [12–14]. In a membrane contactor, gas phase and aqueous phase are separated by a hydrophobic membrane and they flow separately. The membrane provides an interface between gas and water and acts as a distributer of O_3. The

effective interfacial area can be increased tremendously by improving membrane packing density. The volumetric mass transfer coefficient can be 1–2 orders magnitude higher relative to fine bubble contactor [11]. In comparing with conventional contactors, membrane contactor also has advantages such as the avoidance of bubble and foam formation, the reuse of oxygen in the gas phase and the lower energy consumption [15,16].

Nevertheless, most reported membrane contactors for O_3 based on direct ozonation. The application of membrane contactor might be limited for ozone-resistant compounds in advanced wastewater treatment, herbicides removal and micropollutants mineralization. In fact an advanced oxidation process (AOP) may happen in O_3 wastewater treatment process by catalyzing O_3 transforming to hydroxyl free radicals ($\cdot OH$) [17,18]. AOPs have attracted much attention due to their ability on mineralizing refractory organic compounds. O_3 is one of the most studied reagents for producing $\cdot OH$ in laboratory [19–21]. Some ozone-resistant compounds can be easily degraded by $\cdot OH$. The organic degradation can be critically improved by catalytic ozonation process in O_3 wastewater treatment [22–24].

Therefore, combining membrane contact ozonation (MCO) with O_3 based AOPs may improve its oxidation capacity to refractory compounds. Merle et al. combined a membrane contactor with peroxone (O_3/H_2O_2) process for simultaneous micropollutant abatement and bromate minimization. The hybrid process performed better than conventional O_3/H_2O_2 process for both ground water and surface water [25]. Li et al. coated ferrihydrite and active carbon on the surface of hollow fiber membranes in membrane contactor to catalyze O_3 dissolution and transformation to $\cdot OH$, where the removal of *N,N*-diethyl-meta-toluamide in water improved from 30% to 60% [26]. These combinations of membrane contactor and catalytic ozonation improved the oxidation capacity of O_3 process. Considering the high proportion of O_2 in the effluent of an ozonator, it could be a good way to electro-catalytic O_2 to H_2O_2 and implement an O_3/H_2O_2 process by coating conductive catalyzer on the surface of membranes in a membrane contactor.

In this study a novel electro-catalytic membrane contactor was designed. A nickel (Ni) foam plate and a polyvinylidene fluoride (PVDF) hydrophobic membrane were placed in the contactor (Fig. 1). The Ni foam contacted with water phase and acted as a cathode in the reactor, while the PVDF membrane affixed to the Ni foam tightly and contacted with the gas phase. In the electro-catalytic membrane contact ozonation (ECMCO) process, O_2 in the effluent of an ozonator diffuses into aqueous phase through hydrophobic membrane and is electrolytically reduced to H_2O_2 (Eq. (1)); O_3 diffuses from gas phase into aqueous and reacts with H_2O_2 producing $\cdot OH$ (Eqs. (2)–(8)) to degrade organic compounds rapidly.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad (1)$$

$$H_2O_2 \rightleftharpoons H^+ + HO_2^- \qquad (2)$$

$$HO_2^- + O_3 \rightarrow HO_2\cdot + O_3^{-}\cdot \qquad (3)$$

$$HO_2\cdot \rightleftharpoons \cdot O_2^- + H^+ \qquad (4)$$

$$\cdot O-2 + O_3 \rightarrow O_2 + O_3^-\cdot \qquad (5)$$

$$O_3^-\cdot + H^+ \rightleftharpoons HO_3\cdot \qquad (6)$$

$$HO_3\cdot \rightarrow \cdot OH + O_2 \qquad (7)$$

$$O_3 + OH^- \rightarrow HO_2^- + O_2 \qquad (8)$$
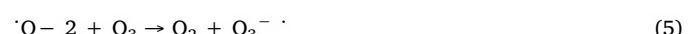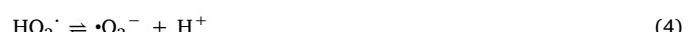
By this design, mass transfer and oxidation efficiency can be mutual promoted: H_2O_2 is produced on the surface of membrane, and O_3 may be rapidly decomposed, which increases the driving force for O_3 transfer; more O_3 molecules can be catalyzed to form $\cdot OH$, and the removal efficiency of ozone-resistant compounds can be improved. Except that, some other advantages can also be achieved, such as (1) some O_2 can be utilized to avoid waste relative to the MCO process; (2) H_2O_2 is produced on site to avoid the risky during the transportation and storage of high concentration H_2O_2 solution; (3) the production of H_2O_2 can be easily controlled by adjusting electric conditions. With these advantages, ECMCO may have the potential on reducing cost and improving oxidation efficiency in processes like advanced wastewater treatment, micropollutant removal and disinfection by-products control.

The objective of this study is to construct an electro-catalytic membrane contractor to improve the organic degradation efficiency by enhancing O_3 mass transfer and implementing O_3/H_2O_2 based AOP. In order to evaluate the oxidation efficiency of ECMCO process, nitrobenzene (NB), an ozone-resistant organic, was chosen as a model contaminant. The efficiency of ECMCO was compared with that of electrolysis and conventional MCO process. The effects of operation conditions including current density, O_3 concentration, gas flow rate and initial pH of the solution were investigated. Mass transfer was investigated and liner sweep voltammtry (LSV) experiments were conducted to evaluate the synergy effects on mass transfer and H_2O_2 production in ECMCO process.

2. Experimental

2.1. Chemicals and materials

NB (AR, > 99.5%), Potassium titanium oxalate (AR), Sulfuric acid (AR, 95% ˜ 98%) was purchased from Sinopharm Chemical Reagent
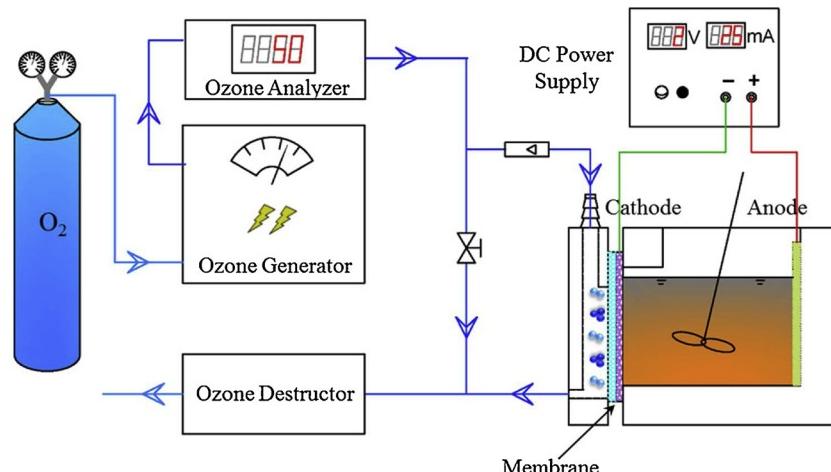

Fig. 1. Schematic of experimental setup.

Table 1
The properties of the PVDF membrane.

Membrane	Thickness (μm)	Porosity (%)	Mean pore size (μm)
ICEQ00010	210	76	0.2

Co., Ltd. (China). Na_2SO_4 (99.5%) and H_2O_2 (30 wt% solution) were from Beijing Chemical works (China). 5,5-Dimethyl-1-pyrroline-*N*-oxide (DMPO) was purchased from Sigma-Aldrich. The PVDF membrane (ICEQ00010) was from Merck (German) (Table 1).

2.2. Experimental setup

The experimental setup is shown in Fig. 1. Flat sheet membrane was employed since it's easy to be assembled and the mechanism will not be different from hollow fiber membrane contactors. The hydrophobic membrane and Ni foam plate were installed in the self-designed module, where the hydrophobic layer contacted with the gas phase and the catalytic layer immerged in the aqueous solution. The aqueous solution contain 0.05 M Na_2SO_4 and the initial concentration of NB was 30 mg/L for all experiments. The volume of the reactor was 120 mL. The anode was RuO_2/Ti mesh and the effective dimension for both anode and cathode were 50 mm × 50 mm. The distance between anode and cathode was 20 mm. The current density ranged from 0.4 to 3 mA/cm^2. The gas flow varied between 25 mL/min and 100 mL/min. The O_3 concentration varied between 0 mg/L and 75 mg/L. When O_3 concentration was 0 mg/L, the ozonator was powered off and pure O_2 was supplied. The initial pH of the solution varied from 2 to 11. Turn on the direct current (DC) power supply and turn off the ozonator to evaluate the performance of electrolysis. Turn off the DC power supply and turn on the ozonator to evaluate the performance of MCO. Turn on the DC power supply and ozonator at the same time to evaluate the performance of ECMCO. And then the removal rate of NB in each process was compared. The initial pH of NB solution was adjusted by adding 1 M H_2SO_4 or 1 M NaOH. The replication of each test was 3, and average value was adopted.

2.3. Analysis methods

The concentration of NB was measured by using High Performance Liquid Chromatography (HPLC, Agilent 1260 Infinity). The concentration of H_2O_2 was measured using potassium titanium oxalate method [27]. The amount of ·OH was analyzed by using electron spin resonance (ESR) method [28], and DMPO was used to trap ·OH.

3. Results and discussion

3.1. The performance of ECMCO on NB removal

In comparing with conventional MCO and electrolysis, ECMCO process exhibited the highest removal rate for NB in 120 min (Fig. 2). The efficiency of electrolysis was the lowest and only 23% of NB was removed in 120 min. The removal efficiency of NB in MCO was much better than electrolysis, and the removal rate was 55% in 120 min. In ECMCO process the removal rate of NB in 120 min was 85%. The removal rate of ECMCO was higher than the summation removal rate of electrolysis and MCO, indicating a synthetic effects in the combination of MCO and electrolysis. The enhancement on NB removal benefited from the production of ·OH in ECMCO process that was further discussed later.

3.2. Mechanism of ECMCO process

The composition of gas phase was changed to evaluate the role each component in gas phase played in ECMCO process, and the
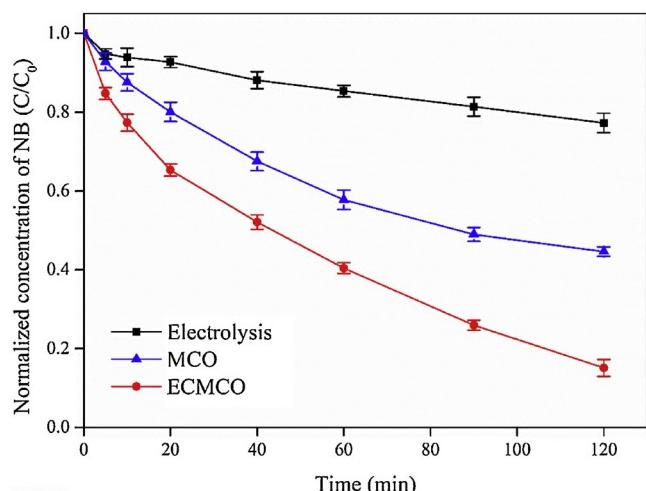
Fig. 2. The removal of NB in different processes (current density of 1 mA/cm^2; gas flow rate of 50 mL/min; O_3 concentration of 50 mg/L; initial pH of 7).
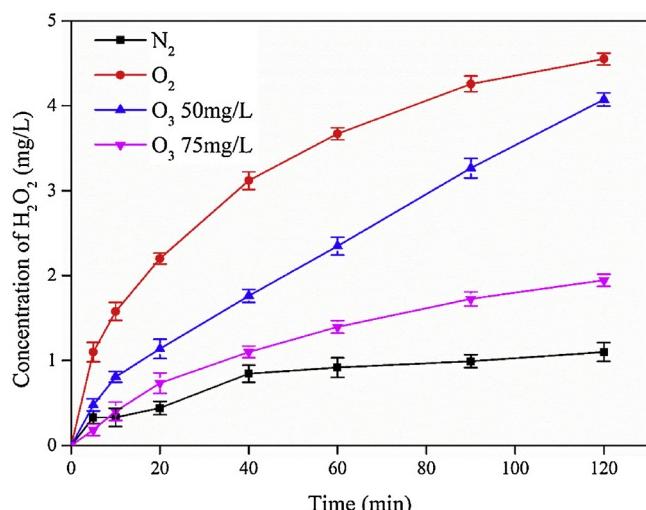
Fig. 3. H_2O_2 concentration with different gases charging (current density of 1 mA/cm^2; gas flow rate of 50 mL/min; initial pH of 7).

corresponding concentrations of H_2O_2 were shown in Fig. 3. The concentration of H_2O_2 was the lowest when pure N_2 was charged due to the insufficient O_2 in the aqueous. And the slight amount of O_2 came from the dissolved O_2 in the initial NB solution and oxygen evaluation reaction at the anode region. When pure O_2 was charged at the gas phase, H_2O_2 concentration was the highest and it increased by 4 times than that when N_2 was charged. It indicated that the O_2 at the gas phase diffused into the aqueous through the hydrophobic layer and was utilized to produce H_2O_2 in the catalytic layer. When the mixture of O_2 and O_3 was charged at the gas phase, H_2O_2 concentration decreased, and it decreased with the increase of O_3 concentration. It indicated that the electrolytically produced H_2O_2 was partially consumed by O_3 which diffused into the aqueous through the hydrophobic layer. Along with the increase of O_3 concentration, the driving force of O_3 was increased due to the larger concentration difference across the membrane. Therefore, more O_3 transferred into the aqueous phase and consumed more H_2O_2.

The production of ·OH in ECMCO process was confirmed by ESR results in Fig. 4. The characteristic peaks in ESR spectra revealed the existence of ·OH in ECMCO process. The intensity of the peaks reflects the relative amount of ·OH to a degree [29]. The amount of ·OH increased in the initial 40 min and then leveled off. In the initial 40 min
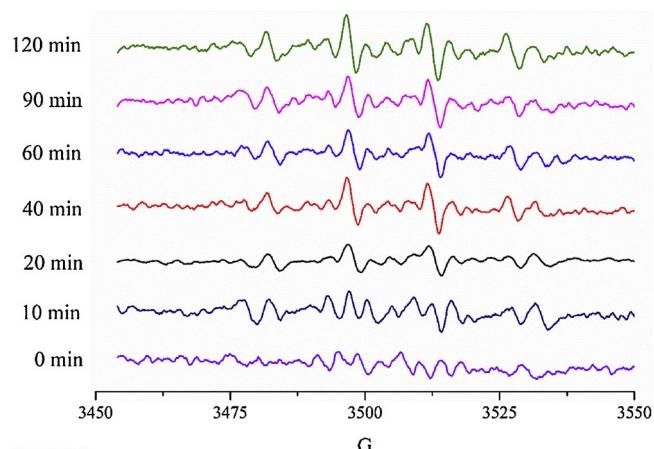
Fig. 4. The ESR spectra with elapsed time (current density of 1 mA/cm^2; gas flow rate of 50 mL/min; O$_3$ concentration of 50 mg/L; initial pH of 7).

the accumulated H$_2$O$_2$ might be insufficient and limited the production of ·OH. After 40 min, the amount of ·OH kept as a constant indicating that enough H$_2$O$_2$ was accumulated in the system while O$_3$ was relatively insufficient. The amount of O$_3$ diffused into aqueous was determined by both driving force and resistance to mass transfer, which was affected by operation conditions that were discussed later.

3.3. Effects of operation conditions

When O$_3$ concentration was 0 mg/L, pure O$_2$ was charged in the gas chamber. The removal rate of NB was just 23% (Fig. 2). H$_2$O$_2$ can hardly react with NB [29,30], so NB was just degraded by electrolysis. The existence of 25 mg/L O$_3$ dramatically increased the removal rate of NB to 79%, while increasing O$_3$ concentration from 25 to 75 mg/L only increased the removal rate from 79% to 93% (Fig. 5(a)). These results

revealed that the existence of ·OH dramatically improved the removal rate of NB. NB reacts slowly with molecule O$_3$ (0.09 $\pm$ 0.02 M^{-1}s^{-1}) and reacts quickly with ·OH (2.2 × 10^8 M^{-1}s^{-1}) [31]. When O$_3$ concentration increased from 25 to 75 mg/L, the removal rates in the former 40 min were no obvious difference, since the electro-produced H$_2$O$_2$ did not accumulate enough and limited the removal of NB. It's in coordination with previous results in Fig. 4. After 40 min, the increased O$_3$ concentration in the gas phase enhanced the driving force of mass transfer through the membrane, which increased the O$_3$ consumption and the ·OH production that facilitated the removal of NB.

The effects of current density on the final removal rate of NB were slight (Fig. 5(b)). The NB removal rates at 120 min were 84%, 85%, 87% and 92% when the current density was 0.4, 1, 2 and 3 mA/cm^2, respectively. The removal rate of NB in former 40 min was evidently enhanced by increasing current density from 0.4 to 3 mA/cm^2. The main reason was that the increase of current density enhanced the accumulation of H$_2$O$_2$ (Fig.S1) and promoted the production of ·OH. Besides, the electrolysis degradation of NB should have been enhanced along with the increase of current density, which also contributed to the significant difference of removal rate in the former 40 min.

The effects of gas flow on NB removal were slight (Fig. 5(c)). The removal rate increased from 77% to 85% when gas flow increased from 25 to 50 mL/min. Mass transfer in membrane contactor follows double-film theory. The resistances for O$_2$ and O$_3$ transfer were in the gas boundary layer, membrane matrix and liquid boundary in sequence. The increased gas flow intensified the turbulence of gas phase and decreased the resistance in gas boundary layer, which facilitated the mass transfer of O$_3$. The increased gas flow might have also improved the mass transfer of O$_2$, which might enhance the production of H$_2$O$_2$ and further promote the mass transfer of O$_3$. While continuous increase of gas flow had no significant improvement on NB removal, since the resistance in water phase boundary layer and membrane matrix might dominate the mass transfer of O$_3$, and the resistance in gas film was negligible [32].

The effects of initial pH value on the removal of NB were shown in
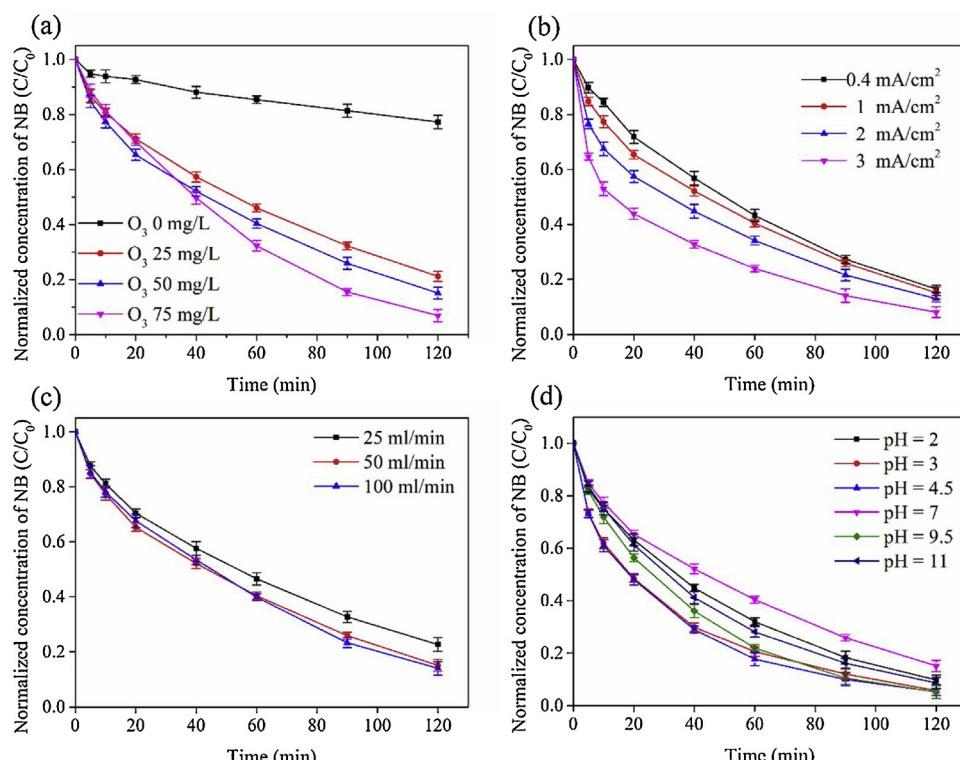
Fig. 5. Operation conditions effects on removal of NB: (a) O$_3$ concentration; (b) current; (c) gas flow rate; (d) initial pH value (current density of 1 mA/cm^2; gas flow rate of 50 mL/min; O$_3$ concentration of 50 mg/L; initial pH of 7).

Fig. 5(d). These results indicated that the ECMCO process performed very well on NB removal in a relative large range of pH. When the initial pH value was 4.5, the removal rate of NB was the highest of 95.7%. And it was the lowest when initial pH value was 7. When initial pH value was lower than 3 or higher than 9.5, the removal rate of NB decreased. The reactions in ECMCO was complicated involving several process and chain reactions (Eq. (2) – (7)). In an acid aqueous solution, the production of H_2O_2 can be enhanced [33], but the existence form of H_2O_2 was also effected by the concentration of H^+. The reaction of H_2O_2 with O_3 is slow, but that of its anion, HO_2^-, is fast. Thus the concentration of HO_2^- determines the chain reaction of producing $\cdot OH$ [34,35]. When initial pH value was 4.5 the amount of HO_2^- might increase due to the enhanced electro-reduction of O_2 to H_2O_2. When the initial pH value was lower than 4.5, the increased concentration of H^+ might limit the amount of HO_2^- (Eq. (2)). Consequently, the removal rate of NB decreased when initial pH value was 2. On the contrary, in an alkalescent aqueous solution, the production of H_2O_2 could be inhibited to a degree, but the amount of HO_2^- might increase due to the equilibrium shifting. Besides, OH^- can react with O_3 producing $\cdot OH$ (Eq. (8)) [36]. When the initial pH value was higher than 9.5, the production of H_2O_2 might be critically inhibited inducing the decrease of removal rate. Furthermore, pH can affect the mass transfer rate of O_3 and the solubility of O_3 in aqueous. Solution pH can therefore have very complex effects on the $\cdot OH$ production in ECMCO process, which may require further investigation.

3.4. Mass transfer of O_3

By measuring O_3 concentrations in the effluent of electro-catalytic membrane contactor and conventional membrane contactor, the mass transfer of O_3 was calculated. These results were shown in Fig. 6. It can be found that the mass transfer of O_3 in ECMCO process was about 2 times higher than that in MCO process. The O_3 residual concentrations in bulk liquid were also tested, and there were no O_3 residual at any time for both processes. It indicated that the O_3 transferred through membrane were totally utilized and the O_3 utilization was 2 times improved by implementing O_3/H_2O_2 based AOP. The enhanced mass transfer rate was due to the intensified reaction of O_3 with HO_2^-. HO_2^- had higher reaction rate constant with O_3 than that of NB [34,37]. O_3 in the liquid phase was consumed rapidly, which increased the concentration difference of O_3 between two sides of the hydrophobic layer and hence improved the driving force for O_3 transfer. Besides, the H_2O_2 is produced just on the surface of the hydrophobic layer, which may promote O_3 mass transfer more effectively than adding H_2O_2 in the
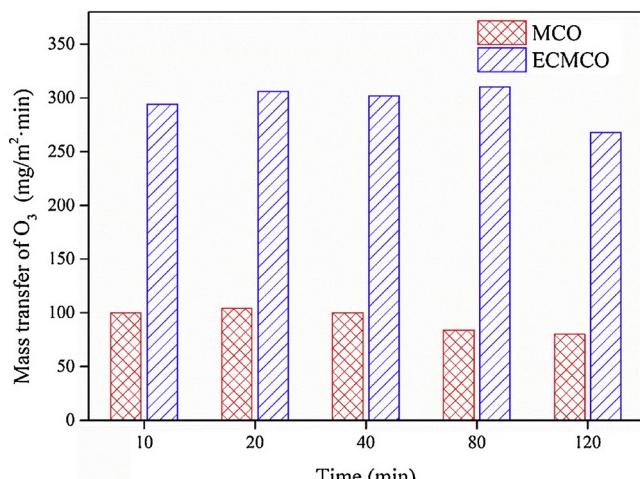
Fig. 6. Mass transfer of O_3 in ECMCO and MCO processes with elapsed time (current density of 25 mA/cm^2; gas flow rate of 50 mL/min; O_3 concentration of 50 mg/L; pH of 7).
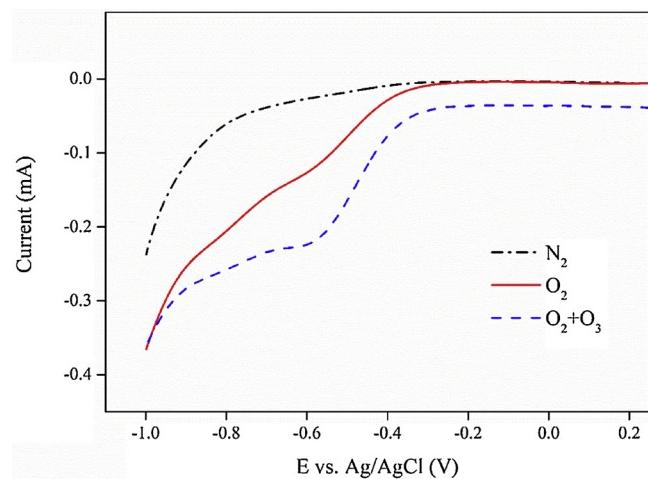
Fig. 7. LSV curves with charging different gases into the gas chamber.

feed.

3.5. LSV experiments

LSV experiments were conducted with charging different gases into the gas chamber (Fig. 7). When pure N_2 was charged, the LSV curves revealed that the hydrogen evolution reaction happened at the potential of -0.8 V vs. Ag/AgCl. When pure O_2 was charged, the reduction current occurred when potential was lower than -0.4 V, where O_2 was electro-reduced to H_2O_2 through the two-electron pathway. When the mixture of O_2 and O_3 was charged in the gas chamber, there was a constant reduction current when voltage ranged from 0.2 V to -0.4 V vs. Ag/AgCl. This reduction current related to the reduction of O_3 [38]. With the existence of O_3, O_2 reduction still occurred at the potential of -0.4 V vs. Ag/AgCl. The reduction current was much stronger in the range of -0.5 to -0.8 V vs. Ag/AgCl than that when pure O_2 was charged in the gas chamber. The enhanced reduction current indicated that the O_3 promoted the production of H_2O_2 from the cathodic reduction of O_2. The dissolved O_3 consumed some HO_2^- rapidly in the catalytic layer, which might enhance HO_2^- releasing from the active site on cathode, so the production of H_2O_2 was facilitated [39]. When the cathodic potential was more negative than -1.0 V vs. Ag/AgCl, the reduction currents were the same for pure O_2 and O_2/O_3 charging. This indicated that the cathodic O_3 reduction was limited as the cathodic potential was getting more negative. This may be because of that the enhanced production of H_2O_2 consumed more O_3, and hence the cathodic reduction of O_3 was limited. This result was corresponding with what was found by Xia et. al. [38]. The LSV experiment results suggested that the existence of O_3 didn't compete with the cathodic reduction of O_2, but O_3 actually facilitated the production of H_2O_2 from O_2 reduction.

All these results illustrated the synthetic effects between electrolysis and membrane contact mass transfer in ECMCO process: the electro-catalytic production of H_2O_2 facilitated the mass transfer of O_3; the existence of O_3 enhanced the production of H_2O_2 from cathodic reduction of O_2. The mutual promotion of H_2O_2 production and O_3 mass transfer determined a high production of $\cdot OH$ and removal rate of NB.

4. Conclusions

A novel ECMCO process was constructed by coupling MCO with peroxone processes. The removal of NB in ECMCO was even faster than the summation of that in MCO and electrolysis due to the production of $\cdot OH$. ECMCO process can be affected by O_3 concentration in the gas phase and current intensity. The effects of gas flow rate were slight. In the former 40 min, the accumulated H_2O_2 was usually low and

dominated the production of ˙OH. While after 40 min, the amount of O_3 transferred turned out to be the limitation for ˙OH production. ECMCO can work in the range of initial pH value of 2 to 11. In ECMCO process, membrane contact mass transfer and electro-catalytic reduction of O_2 were synergistic. The electro-catalytic production of H_2O_2 facilitated the mass transfer of O_3 by 2 times, since O_3 can be rapidly consumed by H_2O_2; and the existence of O_3 enhanced the production of H_2O_2 from cathodic reduction of O_2. Therefore, ECMCO has a great potential to improve the O_3 technology in wastewater treatment by solving two critical issues on the mass transfer of O_3 and the decomposition of O_3 into ˙OH.

Acknowledgement

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcatb.2019.03.015.

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